

MOISTURE-CURABLE, POLYETHER URETHANES
WITH REACTIVE SILANE GROUPS AND THEIR USE
AS SEALANTS, ADHESIVES AND COATINGS

5 CROSS REFERENCE TO RELATED PATENT APPLICATION

This application is a Continuation-In-Part of U.S. Serial Number
10/160,463 filed May 31, 2002.

FIELD OF THE INVENTION

10 The present invention relates to moisture-curable urethanes
containing reactive silane groups and prepared from polyether polyols
having a low degree of unsaturation and to the use of these polyurethanes
as sealants, adhesives and coatings.

15 BACKGROUND OF THE INVENTION

Polyether urethanes containing reactive silane groups, also referred
to as silane-terminated polyurethanes (STPs), and their use as sealants
and adhesives are known and described, e.g., in U.S. Patents 5,554,709;
4,857,623; 5,227,434 and 6,197,912; and WO 02/06367. The silane-
20 terminated polyurethanes may be prepared by various methods. In one
method the silane-terminated polyurethanes are prepared by reacting
diisocyanates with polyether polyols to form isocyanate-terminated
prepolymers, which are then reacted with aminosilanes to form the silane-
terminated polyurethanes. The sealants may also be prepared by reacting
25 unsaturated monools with diisocyanates to form intermediates containing
unsaturated end groups and then converting these unsaturated groups to
alkoxysilane groups by hydrosilylation. In another method the sealants
are prepared in one step by the reaction of polyether diols with
isocyanatosilanes.

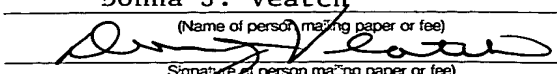
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To be useful as sealants the silane-terminated polyurethanes should have a number average molecular weight of 6000 to 20,000. One method of obtaining this molecular weight is to use polyether diols prepared by the KOH process and having a molecular weight of 2000 to
5 prepare the isocyanate-terminated prepolymers. The presence of urethane groups causes the products to have a high viscosity. To achieve suitable application viscosities, the high viscosity is reduced by the addition of higher amounts of plasticizer and lesser amounts of fillers, resulting in more expensive sealant products.

10 Another method of obtaining high molecular weight sealants is by using high molecular weight polyether diols having a low degree of unsaturation and prepared using special catalysts as described in EP-A 0,546,310, EP-A 0,372,561 and DE-A 19,908,562. When these polyether diols are used, the resulting sealants have excellent tensile
15 strength, but the sealants are too brittle for many applications because the elongation is too low and the 100% modulus is too high.

It is an object of the present invention to provide polyether urethanes that have reactive silane groups and are suitable for use as sealants, adhesives and coatings which possess high tensile strengths
20 and elongations and have a reduced 100% modulus when compared with existing products.

This object may be achieved with the polyether urethanes containing reactive silane groups according to the present invention. These polyether urethanes contain a mixture of polyether urethanes
25 containing two or more reactive silane groups with polyether urethanes containing one reactive silane group. In addition, the polyether urethanes containing two or more reactive silane groups are prepared from high molecular weight polyether polyols having a low degree of unsaturation and the reactive silane groups are incorporated by the use of certain
30 aspartate-functional silanes.

The silane-terminated polyether urethanes according to the invention are suitable for the preparation of sealants or adhesives that have higher tensile strengths and elongations and lower 100% moduli. Due to the fact that these polyether urethanes have a low viscosity, sealant compositions can be formulated with less of the more expensive plasticizers and more of the less expensive fillers, resulting in less expensive sealants.

The preparation of sealants from mixtures of polyfunctional and monofunctional silane-terminated polyurethanes is known and disclosed in U.S. Patents 5,554,709 and 4,857,623 and WO 02/06367. However, these references do not disclose the use of polyether polyols having a low degree of unsaturation and aspartate-functional silanes to prepare the sealants.

The preparation of silane-terminated polyether urethanes from aspartate-functional silanes is disclosed in U.S. Patent 5,364,955 and WO 98/18843. In both of these references the polyethers used to prepare polyether urethanes do not have a low degree of unsaturation. In addition, mixtures of polyfunctional and monofunctional silane-terminated polyurethanes are not disclosed. Finally, in the latter reference the polyethers must contain 15 to 40% by weight of ethylene oxide units.

WO 00/26271 discloses the preparation of silane-terminated polyether urethanes from polyether polyols having a low degree of unsaturation and aspartate-functional silanes. The products are prepared by reacting diisocyanates with high molecular weight polyether diols to form NCO prepolymers, which are then capped with aspartate-functional silanes to form silane-terminated polyether urethanes. This application does not disclose mixtures of disilane-terminated polyether urethanes with polyether urethanes containing one reactive silane group.

U.S. Patent 6,265,517 describes a similar process for preparing silane-terminated polyether urethanes from polyether polyols having a low degree of unsaturation and aspartate-functional silanes. The patent

requires the starting polyol to have a monool content of less than 31 mole%, and teaches that a relatively high monool content is highly undesirable because monools react with isocyanates thereby reducing crosslinking and curing of the prepolymer. The patent also requires the
5 aspartate silanes to be prepared from dialkyl maleates in which the alkyl groups each contain more than four carbon atoms.

EP 0,372,561 discloses polyether urethanes containing reactive silane groups and prepared from polyether polyols having a low degree of unsaturation. In addition, polyether urethanes containing one reactive
10 silane group are disclosed. This application fails to disclose the use of aspartate-functional silanes to incorporate the reactive silane groups.

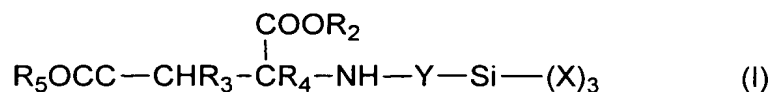
Copending applications, Ser. Nos. 10/160,479, 10/174,039, 10/173,919, and 10/160,364, disclose alkoxysilane-functional polyether urethanes containing a mixture of polyether urethanes containing two or
15 more reactive silane groups with polyether urethanes containing one reactive silane group. The polyether urethanes containing two or more reactive silane groups are prepared from high molecular weight polyether polyols having a low degree of unsaturation.

20 SUMMARY OF THE INVENTION

The present invention relates to moisture-curable, alkoxysilane-functional polyether urethanes containing

a) 20 to 90% by weight, based on the weight of a) and b), of a polyether urethane containing two or more reactive silane groups
25 and one or more polyether segments, wherein the polyether segments have a number average molecular weight of at least 3000 and a degree of unsaturation of less than 0.04 milliequivalents/g, provided that the sum of the number average molecular weights of all of the polyether segments per molecule
30 averages 6000 to 20,000, and wherein the reactive silane groups

are incorporated as the reaction product of an isocyanate group with a compound corresponding to the formula



5

wherein

- X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least two of these groups are alkoxy or acyloxy groups,
- 10 Y represents a linear or branched alkylene group containing 1 to 8 carbon atoms,
- R₂ and R₅ are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less and
- 15 R₃ and R₄ are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less, and
- b) 10 to 80% by weight, based on the weight of a) and b), of a polyether urethane containing one reactive silane group and one or
- 20 more polyether segments having a number average molecular weight of 1000 to 15,000.

The present invention also relates to sealant, adhesive and coating compositions containing these polyether urethanes.

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DETAILED DESCRIPTION OF THE INVENTION

In the moisture-curable, polyether urethanes according to the present invention polyether urethanes a) are present in a minimum amount of at least 20% by weight, preferably 30% by weight and more preferably 40% by weight. The maximum amount of polymers a) is 90%

30 by weight, preferably 80% by weight and more preferably 70% by weight.

Polyether urethanes b) are present in a minimum amount of 10% by weight, preferably 20% by weight and more preferably 30% by weight. The maximum amount of polymers b) is 80% by weight, preferably 70% by weight and more preferably 60% by weight. The preceding percentages are based on the total weight of polyether urethanes a) and b).

Suitable polymers for use as component a) include polyether urethanes containing one or more, preferably one, polyether segment having a number average molecular weight of 3000 to 20,000, preferably 6000 to 15,000 and more preferably 8000 to 12,000. When the polyether segments have a number average molecular weight of 3000, for example, then two or more of these segments must be present so that the number average molecular weights of all of the polyether segments per molecule averages 6000 to 20,000. Polymers a) also contain two or more, preferably two reactive silane groups. The reactive silane groups are incorporated by the reaction of an isocyanate group with a compound corresponding to formula I.

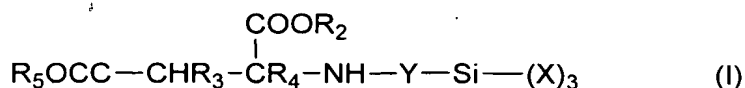
In accordance with the present invention the term "reactive silane group" means a silane group containing at least two alkoxy or acyloxy groups as defined by substituent "X". A silane group containing two or three alkoxy and/or acyloxy groups is considered to be one reactive silane group. Also, a urethane is a compound containing one or more urethane and/or urea groups. These compounds preferably contain one or more urethane groups and may optionally contain urea groups. More preferably, these compounds contain both urethane and urea groups.

Polymers a) may be prepared by several methods. For example, they may be prepared by reacting a high molecular weight polyether containing at least two isocyanate-reactive groups, preferably hydroxyl groups, with an excess of a polyisocyanate, preferably a diisocyanate, to form an NCO prepolymer. The resulting NCO prepolymer is then reacted with an aminosilane corresponding to formula I to form polymers a). Polymers a) may also be prepared by reacting an excess of a polyiso-

cyanate with an aminosilane to form a monoisocyanate and then reacting the resulting intermediate with a high molecular weight polyether to form polymers a).

Suitable aspartate silanes are those corresponding to formula I

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wherein

10 X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least two of these groups are alkoxy or acyloxy groups, preferably alkyl or alkoxy groups having 1 to 4 carbon atoms and more preferably alkoxy groups,

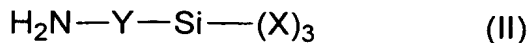
15 Y represents a linear or branched alkylene group containing 1 to 8 carbon atoms, preferably a linear group containing 2 to 4 carbon atoms or a branched group containing 5 to 6 carbon atoms, more preferably a linear group containing 3 carbon atoms and

20 R₂ and R₅ are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably alkyl groups having 1 to 9 carbon atoms, more preferably alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl or butyl groups and

25 R₃ and R₄ are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less, preferably hydrogen.

Especially preferred are compounds in which X represents methoxy, ethoxy groups or propoxy groups, more preferably methoxy or ethoxy groups, and Y is a linear group containing 3 carbon atoms.

30 The compounds of formula I are prepared by reacting aminosilanes corresponding to formula II



with maleic or fumaric acid esters corresponding to formula III



Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl acyloxysilanes corresponding to formula II include 3-aminopropyl-triacyloxysilane, 3-aminopropyl-methyldimethoxysilane; 6-aminohexyl-tributoxysilane; 3-aminopropyl-trimethoxysilane; 3-aminopropyl-triethoxysilane; 3-aminopropyl-methyldiethoxysilane; 5-aminopentyl-trimethoxysilane; 5-aminopentyl-triethoxysilane; 4-amino-3,3-dimethylbutyl-trimethoxysilane; and 3-aminopropyl-triisopropoxysilane. 3-aminopropyl-trimethoxysilane and 3-aminopropyl-triethoxysilane are particularly preferred.

Examples of optionally substituted maleic or fumaric acid esters suitable for preparing the aspartate silanes include the dimethyl, diethyl, dibutyl (e.g., di-n-butyl), diamyl, di-2-ethylhexyl esters and mixed esters based on mixture of these and/or other alkyl groups of maleic acid and fumaric acid; and the corresponding maleic and fumaric acid esters substituted by methyl in the 2- and/or 3-position. The dimethyl, diethyl and dibutyl esters of maleic acid are preferred, while the diethyl esters are especially preferred.

The reaction of primary amines with maleic or fumaric acid esters to form the aspartate silanes of formula III is known and described, e.g., in U.S. Patent 5,364,955, which is herein incorporated by reference.

Suitable polyisocyanates which may be used to prepare polymers a) are known and include monomeric organic diisocyanates represented by the formula, $\text{R}(\text{NCO})_2$, in which R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having a molecular weight of 112 to 1,000, preferably 140 to 400. Preferred

diisocyanates are those represented by the above formula in which R represents a divalent aliphatic hydrocarbon group having from 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having from 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having from 5 to 15 carbon atoms or a divalent aromatic hydrocarbon group having from 6 to 15 carbon atoms.

Examples of suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanato-cyclohexyl)-methane, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanatocyclo-hexyl)-methane, 2,4'-diisocyanato-dicyclohexyl methane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydro-toluylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, 2,4- and/or 4,4'-diphenylmethane diisocyanate and 1,5-diisocyanato naphthalene and mixtures thereof.

Monomeric polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanatomethyl-1,8-octamethylene diisocyanate and aromatic polyisocyanates such as 4,4',4''-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating aniline/formaldehyde condensates may also be used. Also suitable, although less preferred, are polyisocyanate adducts prepared from the preceding monomeric polyisocyanates and containing isocyanurate, uretdione, biuret, urethane, allophanate, iminooxadiazine dione, carbodiimide and/or oxadiazinetrione groups.

Preferred diisocyanates include bis-(4-isocyanatocyclohexyl)-methane, 1,6-hexamethylene diisocyanate, isophorone diisocyanate,

$\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, and 2,4- and/or 4,4'-diphenylmethane diisocyanate. Especially preferred are isophorone diisocyanate, 2,4-toluylene diisocyanate and mixtures of 2,4- and 2,6-toluylene diisocyanate.

Suitable polyols for preparing polymers a) are polyols, in many cases diols. In an embodiment of the invention, the polyethers have a number average molecular weight of at least 3000, in some cases at least 6000 and in other cases at least 8000. Also, the number average molecular weight of the polyethers can be up to 20,000, in some cases up to 15,000 and in other cases up to 12,000. The number average molecular weight of the polyethers can vary and range between any of the values recited above.

The polyethers have a maximum total degree of unsaturation of less than 0.04 milliequivalents/g (meq/g) in some cases less than 0.02 meq/g, in other cases less than 0.01 meq/g and in some situations 0.007 meq/g or less. The amount of unsaturation will vary depending on the method used to prepare the polyether as well as the molecular weight of the polyether. Such polyether diols are known and can be produced, as a non-limiting example, by the propoxylation of suitable starter molecules. As another non-limiting example, minor amounts (up to 20% by weight, based on the weight of the polyol) of ethylene oxide can also be used. If ethylene oxide is used, it can be used as the initiator for or to cap polypropylene oxide groups. Non-limiting examples of suitable starter molecules include diols such as ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6 hexanediol and 2-ethylhexanediol-1,3. Also suitable are polyethylene glycols and polypropylene glycols.

Suitable methods for preparing polyether polyols are known and are described, for example, in EP-A 283 148, US-A 3,278,457, US-A 3,427,256, US-A 3,829,505, US-A 4,472,560. US-A 3,278,458, US-A 3,427,334, US-A 3,941,849, US-A 4,721,818, US-A 3,278,459, US-

A 3,427,335 and US-A 4,355,188. They are preferably prepared using double metal cyanides as catalysts.

5 In addition to the polyether polyols, minor amounts (up to 20% by weight, based on the weight of the polyol) of low molecular weight dihydric and trihydric alcohols having a molecular weight 32 to 500 can also be used. Suitable examples include ethylene glycol, 1,3-butandiol, 1,4-butandiol, 1,6-hexandiol, glycerine or trimethylolpropane. However, the use of low molecular weight alcohols is less preferred.

10 It is also possible in accordance with the present invention to use aminopolyethers instead of the polyether polyols. The aminopolyethers may be prepared by aminating the corresponding polyether polyols in known manner.

When preparing polymers a) from a diisocyanate, a diol and an aspartate silane, the diisocyanate is reacted with the diol at an equivalent ratio of isocyanate groups to hydroxyl groups of approximately 2:1 to form an NCO prepolymer. In addition to the 2/1 adduct of the diisocyanate and diol, minor amounts of higher molecular weight oligomers are also formed, such as the 3/2 adduct, etc. When these oligomers are formed, the reaction mixture also contains a minor amount of unreacted diisocyanate, which can be removed, e.g., by distillation, or which can remain in the reaction mixture.

The NCO prepolymer is then reacted with the aspartate silane at an equivalent ratio of isocyanate groups to amino groups of approximately 1:1. The resulting polyether urethane a) contains the reaction products of the NCO prepolymers with the aspartate silanes and optionally polymers c), which are the reaction products of monomeric diisocyanates with the aspartate silanes. Polymers c) are preferably present in an amount of less than 2% by weight, more preferably less than 1% by weight, based on the weight of polyether urethane a). When polymers c) are present, they are preferably present in an amount of at least 0.1% by weight, more

preferably at least 0.5% by weight, based on the weight of polyether urethane a).

Similarly to polymers a), polymers b) also contain one or more polyether segments, but they only contain one reactive silane group.

- 5 Polymers b) may be prepared by several methods. For example, they may be prepared by reacting a high molecular weight polyether containing one isocyanate-reactive group, preferably a hydroxyl group, with an excess of a polyisocyanate, preferably a diisocyanate. The amount of the isocyanate and polyether is chosen such that the resulting product
10 contains one isocyanate group.

- For example, when reacting a diisocyanate with a monool using equimolar mixtures of the reactants, the resulting product contains an average of one isocyanate group. In addition to the monoisocyanate intermediate, which is the 1/1 adduct of the monool and diisocyanate, the
15 reaction mixture also contains minor amounts of non-functional polymers d), which are formed by the reaction of two molecules of the monool with one molecule of the diisocyanate. The reaction mixture may also contain a minor amount of unreacted diisocyanate, which can be removed, e.g., by distillation, or which can remain in the reaction mixture.

- 20 In accordance with the present invention it is also possible to react additional quantities of the monool with the diisocyanate. When the reaction is carried out in this manner, additional amounts of non-functional polymers d) are formed. These polymers remain in the reaction mixture and function as plasticizers during the subsequent use of the moisture-
25 curable, polyether urethanes according to the invention.

- The reaction mixture containing the monoisocyanate intermediate is reacted with a compound containing an isocyanate-reactive group, preferably an -NH group, and one or more, preferably one reactive silane group to form polyether urethane b). The reaction mixture also contains
30 polymers e), which are the reaction products of any monomeric diisocyanates present in the reaction mixture with the isocyanate-reactive

silanes. Polymers e) are considered a part of polyether urethane b), even though they contain two reactive silane groups.

Non-functional polymers d) are preferably present in an amount of less than 60% by weight, more preferably less than 30% by weight and
5 most preferably less than 10% by weight, based on the weight of polyether urethane b). When polymers d) are present, they are preferably present in an amount of at least 0.1% by weight, more preferably at least 0.5% by weight.

Polymers e) are preferably present in an amount of less than 2% by
10 weight, more preferably less than 1% by weight, based on the weight of polyether urethane b). When polymers e) are present, they are preferably present in an amount of at least 0.1% by weight and more preferably at least 0.5% by weight, based on the weight of polyether urethane a).

Polymers b) may also be prepared by reversing these steps and
15 reacting an excess of a polyisocyanate with an isocyanate-reactive silane and then reacting the resulting intermediate with the high molecular weight polyether. Mixtures of polymers b), d) and e) will also be formed when the process steps are carried out in this order.

Suitable polyisocyanates for preparing the polymers b) are those
20 previously set forth as suitable for preparing polymers a). Monomeric diisocyanates are preferred. Also suitable are the difunctional NCO prepolymers previously set forth for preparing polymers a). If the NCO prepolymer contains high molecular weight polyether segments, then low molecular monools can also be used to prepare the previously described
25 monoisocyanate intermediates.

Suitable monools for preparing polymers b) are polyether monools having a number average molecular weight of 1000 to 15,000, preferably 3000 to 12,000 and more preferably 6000 to 12,000. The polyether monools are prepared by the alkoxylation of monofunctional starting
30 compounds with alkylene oxides, preferably ethylene oxide, propylene oxide or butylene oxide, more preferably propylene oxide. If ethylene oxide

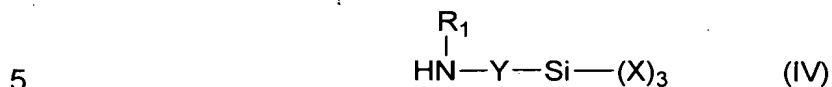
is used, it is used in an amount of up to 40% by weight, based on the weight of the polyether. The polyethers are preferably prepared either by the KOH process or by mixed metal cyanide catalysis. The latter process results in products with low a degree of unsaturation.

- 5 Preferably, the polyethers have a maximum total degree of unsaturation of less than 0.04 milliequivalents/g (meq/g) in some cases less than 0.02 meq/g, in other cases less than 0.01 meq/g and in some situations 0.007 meq/g or less. The amount of unsaturation will vary depending on the method used to prepare the polyether as well as the
- 10 molecular weight of the polyether. These polyether monools are known and can be produced by the methods set forth previously for preparing the polyether polyols, a non-limiting example being by the propoxylation of suitable starter molecules. In a non-limiting example, minor amounts (up to 20% by weight, based on the weight of the polyol) of ethylene oxide can
- 15 be used. As with the polyethers a-i), if ethylene oxide is used, it can be used as the initiator for or to cap the polypropylene oxide groups.

- Examples of suitable starter molecules include aliphatic, cycloaliphatic and araliphatic alcohols, phenol and substituted phenols, such as methanol, ethanol, the isomeric propanols, butanols, pentanols
- 20 and hexanols, cyclohexanol and higher molecular weight compounds such as nonylphenol, 2-ethylhexanol and a mixture of C₁₂ to C₁₅, linear, primary alcohols (Neodol 25, available from Shell). Also suitable are unsaturated alcohols such as allyl alcohol; and hydroxy functional esters such as hydroxyethyl acetate and hydroxyethyl acrylate. Preferred are the higher
- 25 molecular weight monohydroxy compounds, especially nonyl phenol and mixtures of C₁₂ to C₁₅, linear, primary alcohols.

- It is also possible in accordance with the present invention to use monoaminopolyethers instead of the polyether monools. These aminopolyethers may be prepared by aminating the corresponding
- 30 polyether monools in known manner.

Suitable isocyanate-reactive silanes for use in the preceding processes include the previously disclosed aspartate silanes and also those corresponding to the formula

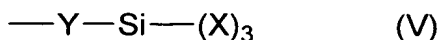


wherein

X and Y are as previously defined and

10 R_1 represents hydrogen or an organic group which is inert to isocyanate groups at a temperature of 100°C or less, preferably hydrogen or an alkyl, cycloalkyl or aromatic group having 1 to 12 carbon atoms and more preferably an alkyl, cycloalkyl or aromatic group having 1 to 8 carbon atoms, or R_1 represents a group corresponding to formula V

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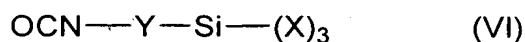


Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl acyloxysilanes of formula IV, which contain primary amino groups, are the compounds of formula II that have previously been described as suitable for preparing the aspartate silanes of formula I.

25 Examples of suitable aminoalkyl alkoxysilanes and aminoalkyl acyloxysilanes of formula IV, which contain secondary amino groups, include N-phenylaminopropyl-trimethoxysilane (available as A-9669 from OSI Corporation), bis-(γ -trimethoxysilylpropyl)amine (available as A-1170 from OSI Corporation), N-cyclohexylaminopropyl-triethoxysilane, N-methylaminopropyl-trimethoxysilane, N-butylaminopropyl-trimethoxysilane, N-butylaminopropyl-triacyloxysilane, 3-(N-ethyl)amino-2-methylpropyl-trimethoxysilane, 4-(N-ethyl)amino-3,3-dimethylbutyl-trimethoxysilane and
30 the corresponding alkyl diethoxy, alkyl dimethoxy and alkyl

diacyloxysilanes, such as 3-(N-ethyl)amino-2-methylpropyl-methyldimethoxysilane.

It is also possible to prepare polymers b) by reacting the polyether in one step with a compound containing isocyanate and alkoxysilane groups corresponding to formula VI



wherein X and Y are as previously defined.

Examples of suitable isocyanatosilanes include 3-isocyanatopropyl-methyldimethoxysilane, 3-isocyanatopropyl-trimethoxysilane and 3-isocyanatopropyl-triethoxysilane. 3-isocyanatopropyl-trimethoxysilane (Silquest Y-5187, available from OSI Corporation) is especially preferred.

When the compounds of formula VI are reacted with a polyether monool to prepare polymers b), then polymers c) and d) are not formed.

Instead of using an aminosilane, it is also possible to prepare polyether urethanes b) by using the hydroxy compound obtained by reacting an aminosilane with a cyclic carbonate such as ethylene or propylene carbonate. The aminosilane may also be replaced with the corresponding thiosilane or the monofunctional adduct of an isocyanatosilane of formula VI with a diol or a diamine.

In accordance with another embodiment of the present invention it is possible to avoid the need for separately preparing a high molecular weight polyether monool by converting a high molecular weight polyether diol into a monool by reacting it with a monoisocyanate. A further alternative for preparing a polyether monool is to react one mole of a diol with a monoacid chloride. Another method for preparing a high molecular weight monool is to react one mole of a monool and one mole of a diol with one mole of a diisocyanate. Either or both of the monool and diol may contain high molecular weight polyether segments. The polyether

monools obtained from these processes can then be used to prepare polymers b) using the previously described processes.

5 If two moles of a diisocyanate are used in the last process, then the resulting product is a monoisocyanate that can be reacted with an isocyanate-reactive compound containing an alkoxy silane group to form polymers b). Another method for forming this monoisocyanate is to react an NCO prepolymer, such as those previously described for preparing polymers a), with a monoalcohol.

10 The polyether monoamines, which have also been described as suitable for preparing polymers b), can be reacted in the same manner as the polyether monools. In addition, they can also be reacted with epoxy silanes to form polymers b).

15 In another embodiment a polyether monool is prepared by the alkoxylation of a hydroxyalkyl (meth)acrylate. The resulting polyether monool is reacted with a monoisocyanate to form an unsaturated intermediate. This intermediate is then reacted with an aminosilane or a thiosilane to incorporate silane groups by a Michael addition.

20 In accordance with a final embodiment of the present invention it is possible to prepare polyether urethanes a) and b) in one step by reacting a mixture of polyether monools and polyether diols with the diisocyanates. Preferably, one mole of diisocyanate is present for each equivalent of hydroxyl groups. The resulting product contains a mixture of NCO prepolymers, monoisocyanate intermediates, non-functional polymers d) and unreacted diisocyanate. The reaction mixture is then reacted with the aspartate silane, which is required to prepare polyether urethanes a), to form a mixture of polyether urethanes a) and b), non-functional polymers d) and polymers c) and e).

25 The compositions of the present invention may be cured in the presence of water or moisture to prepare coatings, adhesives or sealants. 30 The compositions cure by "silane polycondensation" from the hydrolysis of

alkoxysilane groups to form Si-OH groups and their subsequent reaction with either Si-OH or Si-OR groups to form siloxane groups (Si-O-Si).

Suitable acidic or basis catalysts may be used to promote the curing reaction. Examples include acids such as paratoluene sulfonic acid; metallic salts such as dibutyl tin dilaurate; tertiary amines such as triethylamine or triethylene diamine; and mixtures of these catalysts. The previously disclosed, low molecular weight, basic aminoalkyl trialkoxy-silanes, also accelerate hardening of the compounds according to the invention.

The one-component compositions generally may be either solvent-free or contain up to 70%, preferably up to 60% organic solvents, based on the weight of the one-component composition, depending upon the particular application. Suitable organic solvents include those which are known from either from polyurethane chemistry or from coatings chemistry.

The compositions may also contain known additives, such as leveling agents, wetting agents, flow control agents, antiskinning agents, antifoaming agents, fillers (such as chalk, lime, flour, precipitated and/or pyrogenic silica, aluminum silicates and high-boiling waxes), viscosity regulators, plasticizers, pigments, dyes, UV absorbers and stabilizers against thermal and oxidative degradation.

The one-component compositions may be used with any desired substrates, such as wood, plastics, leather, paper, textiles, glass, ceramics, plaster, masonry, metals and concrete. They may be applied by standard methods, such as spraying, spreading, flooding, casting, dipping, rolling and extrusion.

The one-component compositions may be cured at ambient temperature or at elevated temperatures. Preferably, the moisture-curable compositions are cured at ambient temperatures.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

5

EXAMPLES

Preparation of Silane Functional Aspartate (SFA 1)

An aspartate resin was prepared according to U.S. Patent 4,364,955. To a 5 liter flask fitted with agitator, thermocouple, nitrogen inlet and addition funnel with condenser were added 1483g (8.27
10 equivalents) of 3-aminopropyl-trimethoxysilane (Silquest A-1110, available from OSI Corporation). The addition funnel was used to admit 1423.2g (8.27 equivalents) of diethyl maleate over a two hour period. The temperature of the reactor was maintained at 25°C during the addition. The reactor was maintained at 25°C for an additional five hours at which
15 time the product was poured into glass containers and sealed under a blanket of nitrogen. After one week the unsaturation number was 0.6 indicating the reaction was ~99% complete.

Y-5187

3-isocyanatopropyl-trimethoxysilane (Silquest Y-5187, available
20 from OSI Corporation)

A-1110

3-aminopropyl-trimethoxysilane (Silquest A-1110, available from OSI Corporation)

Hydroxy polyether 1

25 A polyoxypropylene diol (Acclaim 12200, (unsaturation = 0.007 meq/g) available from Bayer Corporation) having a functionality of 2 and the equivalent weight set forth in Table 1.

Hydroxy polyether 2

30 A polyoxypropylene diol (Acclaim 8200 (unsaturation = 0.005 meq/g), available from Bayer Corporation) having an OH number of 13.9, an equivalent weight of 4033 and a functionality of 2.

Hydroxy polyether 3

A polyoxypropylene diol (Acclaim 4200 (unsaturation = 0.005 meq/g), available from Bayer Corporation) having an OH number of 29.1, an equivalent weight of 1929 and a functionality of 2.

5 Preparation of hydroxy polyether 4

Nonylphenol (183 g, 0.89 eq) was charged to a stainless-steel reactor. Zinc hexacyanocobaltate-tert-butyl alcohol complex (0.143 g, prepared as described in U.S. Patent No. 5,482,908) was added and the mixture was heated with stirring under vacuum at 130°C for one hour to
10 remove traces of water from the nonylphenol starter. Propylene oxide (5517 g, 125.4 eq) was introduced into the reactor over 6 hours. After the expoide addition was completed, the mixture was heated to 130°C until no further pressure decrease occurred. The product was vacuum stripped and then drained from the reactor. The resulting polyether had an OH
15 number of 8.7, an equivalent weight of 6411, unsaturation = 0.007 meq/g, and a functionality of 1.

Preparation of hydroxy polyether 5

Hydroxy polyether 5 was prepared in the same manner as hydroxy polyether 4 except that 222 g (1.08 eq) of nonylphenol and 5478 g (124.5
20 eq) of propylene oxide were used. The resulting polyether had an OH number of 10.6, an equivalent weight of 5292, unsaturation = 0.006 meq/g, and a functionality of 1.

Preparation of hydroxy polyether 6

Hydroxy polyether 6 was prepared in the same manner as hydroxy
25 polyether 4 except that 407 g (1.97 eq) of nonylphenol and 5293 g (120.3 eq) of propylene oxide were used. The resulting polyether had an OH number of 19.4, an equivalent weight of 2891, unsaturation = 0.005 meq/g, and a functionality of 1.

Preparation of hydroxy polyether 7

30 Hydroxy polyether 7 was prepared in the same manner as hydroxy polyether 4 except that 789 g (3.58 eq) of nonylphenol and 5011 g (113.9

eq) of propylene oxide were used. The resulting polyether had an OH number of 34.6, an equivalent weight of 1619, unsaturation = 0.005 meq/g, and a functionality of 1.

Preparation of Silane Terminated Polyurethanes (STP) 1-9 from aminosilanes

- 5
- A 5 liter round bottom flask was fitted with agitator, nitrogen inlet, condenser, heater and addition funnel. Into the flask were charged the weight of isophorone diisocyanate (IPDI) and the weight of the hydroxy polyether listed in Table 1 and 0.8 g dibutyltin dilaurate. The reaction was
- 10
- heated to 60°C for 3 hours until the theoretical isocyanate content was reached. The weight of the appropriate aminosilane listed in Table 1 was added. The flask was heated at 60°C for an additional 1 hour until no NCO remained as determined by an IR spectrum. 19.9 g of vinyl trimethoxysilane as added as moisture scavenger.

15

Preparation of Silane Terminated Polyurethanes (STP) 10-11 from isocyanatosilanes

- A 1 liter round bottom flask was fitted with agitator, nitrogen inlet, condenser, heater and addition funnel. Into the flask were charged the weight of hydroxy polyether and the weight of 3-isocyanatopropyl-
- 20
- trimethoxysilane (Silquest Y-5187, available from OSI Corporation) listed in Table 1 and 0.05 g dibutyltin dilaurate. The reaction was heated to 50°C for 4 hours until no NCO remained as determined by an IR spectrum. 1.24 g of vinyl trimethoxysilane was added as a moisture scavenger.

Table 1												
STP #	1	2	3	4	5	6	7	8	9	10	11	
Hydroxy Polyether	1	2	3	4	5	6	7	8	9	10	11	
	diol	diol	diol	monool	monool	monool	monool	diol	monool	diol	monool	
Equivalent weight	5861	4033	1929	6411	5292	2891	1619	5817	6411	5817	6411	
Charge weight, g	3631.0	3473.1	3065.8	3664.1	3600.1	3324.3	2933.4	279.2	330.5	238.5	239.9	
Equivalents	0.630	0.860	1.590	0.570	0.680	1.150	1.820	0.048	0.045	0.041	0.033	
IPDI												
Charge weight, g	139.3	191.0	352.5	126.8	150.9	255.0	401.8	10.2	10.0	—	—	
Equivalents	1.260	1.720	3.180	1.140	1.360	2.300	3.620	0.096	0.090	—	—	
Reactive Silane type	SFA 1	SFA 1	SFA 1	SFA 1	SFA 1	SFA 1	SFA 1	A 1110	A1110	Y 5187	Y 5187	
Charge weight, g	229.8	315.2	581.6	209.2	249.0	420.7	664.8	8.0	8.3	11.1	8.9	
Equivalents Charge weight, g	0.630	0.860	1.590	0.570	0.680	1.150	1.810	0.048	0.045	0.041	0.033	
Resin Viscosity mPa.s @ 25°C	73,000	91,000	15,000	16,000	5,500	3,200	1,290	192,000	15,100	4,950	2,800	
								61,500*				
Functionality	2	2	2	1	1	1	1	2	1	2	1	

* 80% solids in diisodecyl phthalate

Formulation of Silane Sealants

The STP's were formulated into sealants using the following typical formulation and procedure. The difunctional STP's were formulated alone and in combination with the monofunctional STP's to demonstrate the effects of these combinations.

Procedure

The following is the standard sealant/adhesive formulation and procedure used to formulate all diol and diol/monool blends. Values given for each formula component are percent by weight of the total formula weight. A high-speed centrifugal mixer was used to mix the formulation components in the steps given below. Each mixing period was one minute in length at a speed of 2200 rpm.

Step 1:

To a clean dry mixing container were charged the following:

STP (blend)	37.5
Plasticizer	17.5
Adhesion Promoter	0.8
Catalyst	0.1
Desiccant	0.5

The ingredients were mixed for one minute in length at a speed of 2200 rpm.

Step 2:

A portion of the filler was added to the mixing container .

Filler 23.6

The ingredients were mixed for one minute at a speed of 2200 rpm.

Step 3:

The remaining filler was added to the mixing container.

Filler 20.0

The ingredients were mixed for one minute in length at a speed of 2200 rpm.

Step 4:

The side of the mix container was scraped and the ingredients were mixed for one additional minute at a speed of 2200 rpm to incorporate all of the filler into the mixture.

5 Step 5:

The resulting product was degassed at 50°C and under full vacuum (>28 mm Hg) for one hour. The material was used immediately.

Exxon Jayflex DIDP was used as the plasticizer. An aminosilane (Silquest A-1120, available from OSI Corporation) was used as the
10 adhesion promoter. A vinyltrimethoxysilane (Silquest A-171, available from OSI Corporation) was used as the desiccant. The filler used was Specialty Minerals Ultra P Flex precipitated calcium carbonate (mean particle size of 0.07 microns). The catalyst used was dibutyltin dilaurate.

The weight ratios of the diols to monools in the STP portion of the
15 sealant formulations were varied as set forth in the following table. The weight ratios are based on the total weight of the STP's in the formulation.

The formulations set forth in the following table were prepared using the preceding procedure for each diol (molecular weights 4000, 8000 and 12000) and for each monool (molecular weights 1000, 3000,
20 6000 and 9000).

Cure and Testing of Silane Sealants

The sealant formulations were cast onto 0.25 inch thick polyethylene sheets and cured at standard conditions of 20 °C, 50% relative humidity for at least two weeks before testing. Tensile strength,
25 percent elongation and 100% modulus were determined according to ASTM D-412. Die "C" tear strengths were determined according to ASTM D-624. The results are set forth in the following table.

Examples 1-96: Properties for the sealants

Example	Disilane STP	Mono- silane STP	Disilane/ Mono- silane Ratio	Die-C Tear (lbs/in)	Ultimate Tensile Strength (psi)	Modulus @ 100% Elongation (psi)	Elonga- tion (%)
1*	8	—	—	49	433	185	269
2*	8	9	80:20	29	371	206	205
3*	8	9	60:40	34	318	252	151
4*	8	9	40:60	27	251	284	93
5*	10	—	—	32	292	188	191
6*	10	11	80:20	28	254	203	158
7*	10	11	60:40	25	201	179	141
8*	10	11	40:60	13	140	187	95
9*	1	—	—	78.0	380	186	338
10	1	4	90:10	62.8	381	165	392
11	1	4	80:20	69.1	347	143	374
12	1	4	70:30	57.0	350	124	477
13	1	4	60:40	59.5	339	106	528
14	1	4	50:50	54.8	309	88	528
15	1	4	40:60	44.0	281	71	528
16	1	4	30:70	38.8	229	47	561
17	1	4	20:80	24.4	163	24	584
18*	1	4	10:90	Product too soft for testing			
19	1	5	90:10	64.2	376	159	390
20	1	5	80:20	58.7	379	148	392
21	1	5	70:30	48.3	363	119	454
22	1	5	60:40	53.9	347	100	533
23	1	5	50:50	53.8	324	81	577
24	1	5	40:60	43.6	283	61	599
25	1	5	30:70	34.4	218	34	659
26	1	6	90:10	56.6	375	155	380
27	1	6	80:20	54.8	396	140	475
28	1	6	70:30	60.8	349	112	460
29	1	6	60:40	62.4	372	92	606
30	1	6	50:50	47.3	292	66	568
31	1	6	40:60	43.5	269	31	710
32	1	6	30:70	Product too soft for processing			
33	1	7	90:10	52.6	363	153	394
34	1	7	80:20	63.4	380	97	638
35	1	7	70:30	62.1	359	123	487
36	1	7	60:40	63.8	388	65	809
37	1	7	50:50	50.4	314	42	784
38	1	7	40:60	Product too soft for testing			
39	2	—	—	54.6	337	222	207

Example	Disilane STP	Mono- silane STP	Disilane/ Mono- silane Ratio	Die-C Tear (lbs/in)	Ultimate Tensile Strength (psi)	Modulus @ 100% Elongation (psi)	Elonga- tion (%)
40	2	4	90:10	57.4	322	200	222
41	2	4	80:20	49.6	335	181	272
42	2	4	70:30	44.0	319	147	317
43	2	4	60:40	37.9	309	141	314
44	2	4	50:50	39.0	297	109	395
45	2	4	40:60	36.1	255	83	370
46	2	4	30:70	31.8	218	65	427
47	2	4	20:80	22.5	165	30	480
48*	2	4	10:90	Product too soft for testing			
49	2	5	90:10	45.4	320	193	222
50	2	5	80:20	25.5	329	181	254
51	2	5	70:30	35.1	306	152	260
52	2	5	60:40	45.5	289	131	310
53	2	5	40:60	36.5	257	83	418
54	2	5	30:70	28.0	216	49	471
55	2	6	90:10	42.2	346	201	238
56	2	6	80:20	50.6	337	180	258
57	2	6	70:30	51.9	332	161	284
58	2	6	60:40	48.8	285	121	323
59	2	6	50:50	41.8	307	99	465
60	2	6	40:60	39.5	241	67	466
61	2	6	30:70	24.2	174	34	546
62	2	7	90:10	51.3	361	197	262
63	2	7	80:20	50.4	329	160	306
64	2	7	70:30	59.7	331	131	380
65	2	7	60:40	52.1	327	112	412
66	2	7	50:50	47.2	285	74	475
67	2	7	40:60		227	42	528
68*	3	—	—	35.6	362		84
69*	3	4	90:10	31.8	353		97
70*	3	4	80:20	30.2	306		97
71*	3	4	70:30	25.1	333	305	115
72*	3	4	60:40	30.7	304	264	124
73*	3	4	50:50	25.5	281	225	138
74*	3	4	40:60	26.5	242	209	120
75*	3	4	30:70	20.5	204	140	159
76*	3	5	90:10	31.7	334		80
77*	3	5	80:20	28.3	312		90
78*	3	5	70:30	29.1	304		99
79*	3	5	60:40	22.7	277	264	107
80*	3	5	50:50	26.0	253		109
81*	3	5	40:60	24.4	239	188	138

Example	Disilane STP	Mono-silane STP	Disilane/Mono-silane Ratio	Die-C Tear (lbs/in)	Ultimate Tensile Strength (psi)	Modulus @ 100% Elongation (psi)	Elongation (%)
82*	3	5	30:70	22.6	200	143	154
83*	3	6	90:10	36.2	351		95
84*	3	6	80:20	22.5	336		109
85*	3	6	70:30	24.0	328	302	115
86*	3	6	60:40	35.9	289	266	114
87*	3	6	50:50	27.0	282	218	149
88*	3	6	40:60	23.7	257	173	181
89*	3	6	30:70	22.4	211	126	209
90*	3	7	90:10	32.6	341	311	102
91*	3	7	80:20	28.9	321		105
92*	3	7	70:30	32.5	315	272	130
93*	3	7	60:40	28.5	285	222	156
94*	3	7	50:50	29.6	297	197	187
95*	3	7	40:60	31.3	254	155	212
96*	3	7	30:70	20.3	187	87	258

* Comparison Example

The properties set forth in the table demonstrate the advantages obtained for the sealants according to the invention. The sealants

- 5 according to the invention, which contain difunctional STP's prepared from aspartate-fucntional silanes, provide a much lower modulus at 100% elongation while maintaining or improving the values for ultimate tensile strength and elongation.

- 10 As shown in Table 1 when monofunctional STP's are blended with a difunctional STP prepared from a primary aminosilane (Examples 1-4) or a difunctional STP prepared from an isocyanatosilane, the modulus at 100% elongation to increases and the elongation decreases. To the contrary when monofunctional STP's are blended with the disilane STP's according to the invention, the modulus decreases and the elongation
- 15 increases.

Comparison Examples 68-96 demonstrate that when the molecular weights of the polyether segments are less than 6000, the sealants have inferior properties, especially a low elongation.

Although the invention had been described in detail in the foregoing for the purpose of illustration, it was to be understood that such detail was solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the

5 invention except as it may be limited by the claims.